

COATINGS. ENAMELS

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PIGMENTS BASED ON IRON AND COBALT MOLYBDOPHOSPHATES FOR LOW-MELTING ENAMELS

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The possibility of using pigments based on iron and cobalt molybdophosphates for synthesis of low-melting enamels is demonstrated.

Enameling of metals using tinted low-melting glazes is implemented to protect metals as well as for color decoration and production of ornaments. The development of such enamels involves searching for relatively inexpensive and intensely coloring pigments of a wide color range, resistant at a temperature around 900°C. Currently used pigments as a rule are based on oxides of transitional metals and various spinels [1, 2]. The main disadvantages of such pigments are high cost, substantial consumption of energy in synthesis, and relatively high consumption of chromophores to obtain an intense color.

Pigments that may be promising are molybdophosphates of the iron triad elements [3]. The structural specifics of oxometallates make it possible to reduce the consumption of chromophores while preserving a high intensity of tinting of enamels.

The purpose of our study was to consider possibilities of using iron and cobalt molybdophosphates for tinting low-melting enamels.

Heteropolysalts were produced using two methods: on the basis of acid and on the basis of molybdenum oxide. The first method is based on reaction of 12-molybdophosphoric acid with cobalt and iron salts. Compared with the production of heteropolysalts based on acid, synthesis based on molybdenum oxide is more economic. This method allows for producing pigments using waste generated by the light-engineering industry. The technological scheme of synthesis of molybdophosphates of the iron triad elements based on molybdenum oxide is simple enough and can be included in recycling waste generated by the production of incandescent lamps. The stage of producing a heteropolysalt is of

special significance. In the development of technological regulations for synthesis, special attention should be paid to maintaining the temperature regime and controlling the medium acidity [4].

The iron and cobalt molybdophosphates obtained by us contain around 5% (here and elsewhere mass content) chromophore (Co^{2+} , Fe^{2+} , Fe^{3+}), whereas traditional pigments contain, for instance 71% Co_2O_3 .

We investigated the precipitation of synthesized pigments on inorganic carriers such as MgO , ZnO , Al_2O_3 , quartz sand, TiO_2 , milled porcelain, and natural fillers (tremolite $\text{Ca}_2\text{Mg}_5[\text{OH}]_2[\text{Si}_4\text{O}_{11}]_2$ and diopside $\text{CaMg}[\text{SiO}_2]_2$, wollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$, and silica gel, which makes it possible to additionally reduce 3–5 times the consumption of pigment. The intensity of precipitation of cobalt and iron molybdophosphates in the specified sequence increases and depends on the nature of physicochemical reactions, in particular, and is determined by the acid-base properties of the filler. There is virtually no precipitation on thermodynamically stable structures with a well formed crystalline phase (MgO , ZnO , Al_2O_3). A modification of surface properties, for instance, an increase in acidity and porosity facilitates physicochemical reactions of the pigment with the filler. Thus, precipitation of pigment on tremolite and diopside is more intense and precipitation on wollastonite and silica gel is maximum.

The results of studying the relationship between color purity and the weight of silica gel filler are shown in Fig. 1. As the weight part of the filler (silica gel) increases, the color purity monotonically decreases.

The performed calculation indicates that the optimum quantity of filler is about 5 g per 1 g of pigment. The color of cobalt and iron salts is determined by the $d-d$ transition and

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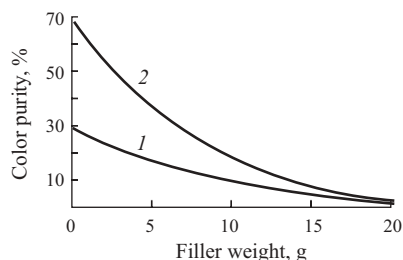


Fig. 1. Dependence of color purity on filler weight: 1 and 2) cobalt (II) 11-molybdophosphate and iron (III) 12-molybdophosphate, respectively.

is within the range of 455–460 nm for cobalt salt and 570–575 nm for iron salt.

Pigments based on heteropolycompounds are resistant to ultraviolet radiation and promising for the development of contemporary materials.

Iron and cobalt molybdophosphates by themselves or deposited on natural silicate fillers were used to tint enamels. Using 0.5–4.0% iron and cobalt salts makes it possible to obtain intensely colored enamels. The tinting persists under high-temperature treatment (about 900°C), which makes it possible to use these pigments in low-melting glazes.

Enamel was produced using the well-known composition of high-lead crystal glass (%): 55.0–60.0 PbO, 30.0–35.0 SiO₂, 5.0–10.0 (K₂O + Na₂O), 0.2–0.5 As₂O₃, 0.1–1.0 Co₂H₃[PMo₁₁O₃₉] · 20H₂O · 3HCl, 4.0–5.0 filler [5]. To prepare enamel, the initial components were mixed and ground in a porcelain mortar. The batch was poured into a

crucible (1/2 of the crucible volume) and melted in a muffle furnace at a temperature of 1150–1200°C. Non-tinted ready enamel was milled and pigment was added. The enamel was deposited at a temperature of 900°C.

When heteropolycompounds are introduced into enamels, the color of the initial pigment is preserved and provides for intense coloring of enamels in the blue-violet range in the case of cobalt molybdophosphates and in the yellow range in the case of iron molybdophosphates. Using pure iron and cobalt molybdophosphates makes it possible to obtain clear enamels and introducing salts precipitated on natural fillers yields opacified enamels.

Thus, the possibility of using iron and cobalt molybdophosphates as pigments is demonstrated. The use of obtained pigments makes it possible to lower the cost of enamel production.

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